Cu-Based Bulk Glass Formation in the Cu-Zr-Ga Alloy System and Their Mechanical Properties

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The thermal stability, glass-forming ability (GFA) and mechanical properties of a new Cu-based glassy alloy in Cu-Zr-Ga ternary system have been investigated. The supercooled liquid region $\Delta T_x (= T_x - T_g)$ exceeding 40 K and reduced glass transition temperature (T_g/T_l) above 0.59 are obtained simultaneously in the composition range from 2.5 to 7.5%Ga and 37.5 to 42.5%Zr, and the highest T_g/T_l is 0.62 for $\text{Cu}_{52.5}\text{Zr}_{42.5}\text{Ga}_5$ and $\text{Cu}_{55}\text{Zr}_{40}\text{Ga}_5$ alloys. The Cu-based Cu-Zr-Ga glassy alloys are formed in a rod form with a diameter up to 2.0 mm by the copper mold casting. The bulk glassy alloys exhibit good mechanical properties of 550–580 for Vicker's hardness (H_v), 105–111 GPa for Young's modulus (E), 1910–2130 MPa for compressive fracture strength ($\sigma_{c,f}$), and 0.2–0.5% for plastic elongation. The GFA of Cu-based Cu-Zr-Ga glassy alloys is more closely related to T_g/T_l values rather than ΔT_x . The present new Cu-based bulk glassy alloys are expected to be developed as another type of bulk structural material with higher strength combined with good ductility.

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1. Introduction

It is known that amorphous alloys have characteristic physical and chemical properties such as high strength, high corrosion resistance and good soft magnetic properties, which are significantly different from the corresponding crystalline alloys.¹⁾ However, the requirement of rapid solidification has lead to strict limitation of their material shape to ribbons, wires and powders and its limitation has restricted further extension of their application fields. Since the findings of glassy-type alloys with a large supercooled liquid region in Mg-Ce-Ni²⁾ and La-Al-Ni³⁾ systems, followed by the successes of producing bulk glassy alloys in the Ln-⁴⁾ (Ln=lanthanide metals) and Mg-⁵⁾ based systems by the copper mold casting method, much attention has been paid to the development of new alloy systems with high glass-forming ability (GFA). As a result, bulk glassy alloy systems have been widely extended to Zr-,^{6,7)} Fe-,⁸⁾ Pd-Cu-,⁹⁾ Co-,¹⁰⁾ Cu-Ti-¹¹⁾ Ni-Zr-¹²⁾ and Ni-Nb-^{13–17)} based alloys. However, there had been no data on the formation of Cu-based bulk glassy alloys which were defined as the alloy containing more than 50 at%Cu. In 2001, we have reported that the Cu-based bulk glassy alloys in Cu-Zr-Ti and Cu-Hf-Ti ternary systems are formed in the thickness range up to of 4 mm, and their alloys possess high strength and good ductility.^{18–20)} These mechanical properties are considerably better than those for Zr-based bulk glassy alloys.^{21,22)} Although a number of Cu-based bulk glassy alloys have been developed in Cu-(Zr,Hf)-Ti,²³⁾ Cu-Zr-Ti-Be,²⁴⁾ Cu-Zr-Ti-(Fe,Co,Ni)²⁵⁾ and Cu-(Zr or Hf)-Ti-(Nb,Ta)^{26–28)} systems, it is important to search for a new ternary Cu-based bulk glassy alloys for future development as a high strength materials. Recently, we have also reported that addition of Al to Cu-Zr alloys was effective for the increase in GFA as well as for the stabilization of supercooled liquid. The Cu-based bulk glassy alloys of 3 mm in thickness are formed in Cu-Zr-Al ternary system and they also exhibit good mechanical properties.²⁹⁾ Considering the

similarities of atomic radius and atomic electronic negativity between Al and Ga elements belonging to the same group number in the periodic table, similar bulk glassy alloys are also expected to be formed in Cu-Zr-Ga system. This paper intends to present the composition dependence of thermal stability of the glassy Cu-Zr-Ga alloys, and the maximum thickness, mechanical properties and fracture behavior of the Cu-based bulk glassy alloys. The reason for the high glass-forming ability in the ternary system is also discussed.

2. Experimental Procedure

Multi-component Ni-based alloy ingots with nominal composition of $\text{Cu}_{100-x-y}\text{Zr}_x\text{Ga}_y$ were prepared by arc melting the mixtures of pure Cu, Zr and Ga metals in a Ti-gettered argon atmosphere. The purity of metals was over 99.9 mass%. Alloy ingots were re-melted four times to ensure chemical homogeneity. The mass losses were measured for each ingot after melting and were less than 0.1 mass%. The glassy alloy was produced by copper mold casting for bulk cylindrical rods with diameters up to 3 mm and by melt spinning for ribbons with a cross section of $0.02 \times 1.5 \text{ mm}^2$. The glassy phase was identified by X-ray diffraction and thermal stability was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K/s. The melting and liquidus temperatures were measured with a differential thermal analyzer (DTA) at a heating rate of 0.17 K/s. Vicker's hardness was measured using a microhardness tester under a load of 50 g. Mechanical properties were measured with an Instron testing machine. The gauge dimension of specimens was 1.5 or 2 mm in diameter and 3 or 4 mm in height for compressive test, and the strain rate was $5 \times 10^{-4} \text{ s}^{-1}$. The fracture surface was examined by scanning electron microscopy (SEM).

Fig. 1 DSC curves of melt-spun $\text{Cu}_{60-x}\text{Zr}_{40}\text{Ga}_x$ ($x = 0$ to 10 at%) glassy alloys.

Fig. 2 DTA curves of melt-spun $\text{Cu}_{60-x}\text{Zr}_{40}\text{Ga}_x$ ($x = 0$ to 10 at%) glassy alloys.

Fig. 3 Changes in the liquidus temperature (T_l) and reduced glass transition temperature (T_g/T_l) as a function of Ga content for melt-spun $\text{Cu}_{60-x}\text{Zr}_{40}\text{Ga}_x$ ($x = 0$ to 10 at%) glassy alloys.

3. Results and Discussion

The X-ray diffraction patterns showed that the melt-spun ribbons of the $\text{Cu}_{100-x-y}\text{Zr}_x\text{Ga}_y$ ($x = 30$ to 60, $x = 0$ to 10) alloys are composed of a single glassy phase. Figure 1 shows DSC curves of the melt-spun $\text{Cu}_{60-x}\text{Zr}_{40}\text{Ga}_x$ ($x = 0$ to 10) glassy alloys. As marked with the glass transition temperature (T_g) and crystallization temperature (T_x), it is noticed that the glass transition and supercooled liquid region ($\Delta T_x = T_x - T_g$) are observed in the Ga concentration range of 0 to 10 at%. As the Ga content increases, T_g and T_x gradually increases, and the increases ratio is considerably larger for T_g , resulting in the ΔT_x gradually decreases from 60 K at $x = 0$ to 28 K at $x = 10$. Figure 2 shows DTA curves of the $\text{Cu}_{60-x}\text{Zr}_{40}\text{Ga}_x$ ($x = 0$ to 10) alloys. The endothermic peak due to melting is observed for all the alloys and the melting reaction appears to occur through a single stage for the $x = 0$ to 5 alloys. Based on the data shown in Fig. 2, the liquidus temperature (T_l) and the reduced glass transition temperature (T_g/T_l) of the $\text{Cu}_{60-x}\text{Zr}_{40}\text{Ga}_x$ ($x = 0$ to 10) alloys were plotted as a function of Ga content in Fig. 3. It is clearly seen that T_l shows a minimum value of 1193 K for $x = 5$ alloy, indicate that a eutectic composition in the ternary system is located in the vicinity of $x = 5$. As a result, the 5%Ga alloy exhibits a maximum T_g/T_l of 0.617. It is thus concluded that the addition of 5%Ga to Cu-Zr glassy alloys is effective for an increase in T_g/T_l .

We further examined the effect of Zr content on the thermal stability of supercooled liquid in the alloy series of $\text{Cu}_{95-x}\text{Zr}_x\text{Ga}_5$. As shown for the DSC curves of the $\text{Cu}_{95-x}\text{Zr}_x\text{Ga}_5$ ($x = 35$ to 50) alloys in Fig. 4, the glass transition phenomenon in conjunction with a supercooled liquid region is observed in a wide Zr content range of 35 to 50 at%. The T_g and T_x decrease monotonously with increasing Zr content, and the ΔT_x value increases monotonously from 39 to 57 K with increasing Zr content to 50 at%. Figure 5 shows the T_l and the T_g/T_l as a function of Zr content for the $\text{Cu}_{95-x}\text{Zr}_x\text{Ga}_5$ ($x = 35$ to 50) glassy alloys. The lowest T_l at about 42.5%Zr causes the highest T_g/T_l of 0.618, and the

further increase in Zr content results in a significant decrease in T_g/T_l . Here, it is noticed that the large ΔT_x exceeding 40 K and high T_g/T_l over 0.59 are simultaneously obtained in the $\text{CuZr}_{37.5-42.5}\text{Ga}_{2.5-7.5}$ alloys, indicating that the Cu-based ternary alloy has high thermal stability of supercooled liquid and high GFA.^{30,31)}

Figure 6 shows X-ray diffraction patterns of the cast rods of composition $\text{Cu}_{52.5}\text{Zr}_{42.5}\text{Ga}_5$, $\text{Cu}_{55}\text{Zr}_{40}\text{Ga}_5$, $\text{Cu}_{57.5}\text{Zr}_{40}\text{Ga}_{2.5}$, and $\text{Cu}_{52.5}\text{Zr}_{40}\text{Ga}_{7.5}$. The rods have diameters of 1.5 and 2.0 mm, respectively. No distinct crystalline peaks are observed for the all samples, indicating the formation of a glassy phase without crystallinity in the diameter range up to 2.0 mm. From the DSC curves of the cast glassy alloy rods with diameters of 1.5 and 2.0 mm, it was confirmed that the T_g , T_x and heat of crystallization were nearly the same among the bulk and ribbon samples, being consistent with the result obtained by X-ray diffraction. Table 1 summarizes the thermal properties and glass-forming ability of the Cu-Zr-Ga glassy alloys. As described above, the Cu-Zr-Ga glassy alloys exhibited a high thermal stability of the supercooled liquid and the high GFA leading to the formation of the bulk glassy rods with diameters up to 2.0 mm. The reason for the larger ΔT_x and high T_g/T_l for the Cu-Zr-Ga glassy alloy is discussed in the framework of the three empirical rules^{30,31)} for the achievement of high GFA. The three empirical rules are (1) multi-component consisting of more than three elements, (2) significant atomic size mismatches among the main constituent elements, and (3) suitable negative heats of mixing their elements. The atomic sizes change in the order of $\text{Zr} > \text{Ga} > \text{Cu}$ and the atomic size ratio is 1.25 for Zr/Cu, 1.14 for Zr/Ga and 1.10 for Ga/Cu.³²⁾ Furthermore, the heats of mixing have been estimated to be -23 kJ/mol for Cu-Zr, -40 kJ/mol for Zr-Ga and -1 kJ/mol for Cu-Ga.³³⁾ Thus, the data on the atomic size ratios and the heats of mixing indicate that the present Cu-based alloy system satisfy the three empirical rules, leading to a high thermal stability of the supercooled liquid against crystallization and the high GFA. The mechanism for the stabilization of supercooled liquid for the alloys satisfying the three

Fig. 4 DSC curves of melt-spun $\text{Cu}_{95-x}\text{Zr}_x\text{Ga}_5$ ($x = 35$ to 50 at%) glassy alloys.

Fig. 5 Changes in the liquidus temperature (T_l) and reduced glass transition temperature (T_g/T_l) as a function of Zr content for melt-spun $\text{Cu}_{95-x}\text{Zr}_x\text{Ga}_5$ ($x = 35$ to 50 at%) glassy alloys.

Fig. 6 X-ray diffraction pattern of the cast Cu-Zr-Ga alloy rod with the diameters of 1.5 and 2.0 mm.

Table 1 Thermal stability and critical sample thickness (t_c) of Cu-Zr-Ga glassy alloys.

Composition (at%)	T_g (K)	T_x (K)	ΔT_x (K)	T_l (K)	T_g/T_l	t_c (mm)
$\text{Cu}_{52.5}\text{Zr}_{42.5}\text{Ga}_5$	733	777	44	1187	0.618	2.0
$\text{Cu}_{55}\text{Zr}_{40}\text{Ga}_5$	736	779	43	1193	0.617	2.0
$\text{Cu}_{42.5}\text{Zr}_{40}\text{Ga}_{7.5}$	744	777	33	1218	0.610	1.5
$\text{Cu}_{57.5}\text{Zr}_{40}\text{Ga}_{2.5}$	723	776	53	1198	0.604	1.5
$\text{Cu}_{57.5}\text{Zr}_{37.5}\text{Ga}_5$	745	785	40	1241	0.601	1.0
$\text{Cu}_{55}\text{Zr}_{42.5}\text{Ga}_{2.5}$	709	762	53	1199	0.591	1.0

empirical rules has been described in previous papers and reviews.^{30,31} It is also noticed that the ΔT_x , T_g/T_l and critical sample thickness (t_c) of the Cu-Zr-Ga bulk glassy alloys are 33–53 K, 0.59–0.62 and 1.0–2.0 mm respectively. The relation among ΔT_x , T_g/T_l and t_c for the Cu-based ternary glassy alloys, indicates that the GFA is not directly related to ΔT_x and depends strongly on T_g/T_l .

Figure 7 shows the compressive stress-strain curve of the glassy alloys rods. It is seen that the glassy alloys exhibit high fracture strengths of above 1900 MPa and the distinct plastic

Fig. 7 Compressive stress-elongation curves of cast (a) $\text{Cu}_{52.5}\text{Zr}_{42.5}\text{Ga}_5$, (b) $\text{Cu}_{55}\text{Zr}_{40}\text{Ga}_5$, (c) $\text{Cu}_{52.5}\text{Zr}_{40}\text{Ga}_{7.5}$ and (d) $\text{Cu}_{57.5}\text{Zr}_{40}\text{Ga}_{2.5}$ glassy alloy rod with the diameters of 1.5 and 2.0 mm.

Table 2 The mechanical properties of f Cu-Zr-Ga bulk glassy alloys.

Composition (at%)	$\sigma_{c,f}$ (MPa)	E (GPa)	$\epsilon_{c,p}$ (%)	H_V
$\text{Cu}_{52.5}\text{Zr}_{42.5}\text{Ga}_5$	1940	105	0.2	552
$\text{Cu}_{55}\text{Zr}_{40}\text{Ga}_5$	2025	109	0.2	565
$\text{Cu}_{42.5}\text{Zr}_{40}\text{Ga}_{7.5}$	2130	111	0.3	581
$\text{Cu}_{57.5}\text{Zr}_{40}\text{Ga}_{2.5}$	1910	105	0.5	547

strains over 0.1%. Table 2 summarizes the mechanical properties of the Cu-Zr-Ga bulk glassy alloy rods. The Cu-Zr-Ga bulk glassy alloys possess good mechanical properties, *i.e.*, compressive fracture strength ($\sigma_{c,f}$) of 1910–2130 MPa, Young's modulus (E) of 105–111 GPa, compressive plastic elongation ($\epsilon_{c,p}$) of 0.2–0.5% and Vickers hardness (H_V) of 547–581. It is noticed that the $\sigma_{c,f}$, E and H_V show a distinct dependence, *i.e.*, a gradual decrease in these strength values with decreasing T_g . It is interpreted that the T_g of the glassy alloys reflects the bonding force among the constituent elements.³⁴ The fracture behavior and fracture surface appearance are exemplified in Fig. 8 for the $\text{Cu}_{52.5}\text{Zr}_{42.5}\text{Ga}_5$ glassy alloy rod. The fracture occurs along the maximum

Fig. 8 Fracture surface appearance of the cast $\text{Cu}_{52.5}\text{Zr}_{42.5}\text{Ga}_5$ glassy alloy rod with a diameter of 2.0 mm.

shear plane which is declined by about 45 degrees to the direction of applied load (Fig. 8(a)), and the fracture surface consists mainly of well developed vein pattern (Fig. 8(b)). The feature of the fracture morphology is the same as that for the other bulk glassy alloys indicates that the present Cu-based bulk glassy alloys with much higher fracture strength are in a ductile state.

4. Summary

We examined the effect of Ga addition on the glass-forming ability, thermal stability and mechanical properties of Cu-Zr glassy alloys, with the aim of synthesizing a bulk glassy alloy with high strength in the Cu-based Cu-Zr-Ga ternary system. The results obtained are summarized as follows.

- (1) In the $\text{Cu}_{60}\text{Zr}_{40-x}\text{Ga}_x$ glassy alloys ($x = 0-10$), T_g and T_x increase monotonously with increasing Ga content, while the ΔT_x decreases monotonously from 60 K at 0%Ga to 28 K at 10%Ga. The T_g/T_1 shows a maximum value of 0.617 at 5%Ga because of the minimum T_1 value of 1193 K at 5%Ga.
- (2) The T_g and T_x of the $\text{Cu}_{95-x}\text{Zr}_x\text{Ga}_5$ glassy alloys decrease monotonously with increasing Zr content while the ΔT_x increases monotonously. The ΔT_x is in the range from 39 K at 35%Zr to 57 K at 50%Zr. The T_1 shows a minimum of 1187 K at 42.5%Zr, leading to a maximum T_g/T_1 of 0.618 at 42.5%Zr.
- (3) Bulk glassy alloy rod with diameters up to 2.0 mm was formed for $\text{Cu}_{52.5}\text{Zr}_{42.5}\text{Ga}_5$ and $\text{Cu}_{50}\text{Zr}_{40}\text{Ga}_5$ alloy by copper mold casting. The glass-forming ability of Cu-based Cu-Zr-Ga alloys is more closely related to T_g/T_1 values rather than ΔT_x .
- (4) The bulk glassy alloy exhibits good mechanical properties, *i.e.*, Vicker's hardness of 547–581, Young's modulus of 105–111 GPa, compressive fracture strength of 1910–2130 MPa, and plastic elongation of 0.2–0.5%.

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